Vibrational spectra of NdF_3 crystal

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Keywords: trifluorides, tysonite structre, Raman spectroscopy, Infrared spectroscopy

Running head: Vibrational spectra of NdF_3 crystal

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The vibrational spectroscopy investigation of phase transitions in NdF_3 crystal is reported. Spectra were obtained in temperature range from 300 to 10 K. It has been shown that, down to 10K, the orthorhombic tysonite structure of NdF_3 trifluoride remains stable.

Introduction

The NdF_3 crystal belong to the rare-earth trifluoride crystals with the tysonite structure ReF_3 (*R*e = La, Ce, Pr, Nd, space group $P\bar{3}c1$, $Z = 6$), which are extensively studied due to their wide applications in fiberoptics, as an active medium of solid-state lasers, sensors and scintillators [1-5]. Unit cell structure of NdF_3 crystal [6] is shown in Fig. 1. According to [7, 8] ReF_3 crystals with tysonite structure undergoes a structural phase transition to high-pressure phase Cmma around 20 GPa. On the other hand, the quantum mechanical simulations [9] and in situ X-ray diffraction [10] shows less-distorted I4/mmm structure for high-pressure phase of LaF_3 crystal. The crystal structure of La, Ce, Pr and Nd triflourides is stable until melting [10]. The melting point of NdF_3 crystal is 1410 K.

The aim of this work was to perform the investigation of vibrational spectra of NdF_3 crystal in a wide temperature and pressure range looking for some features of structural phase transitions.

Experimental

Single crystals of NdF_3 were grown by Bridgeman– Stockbarger method at the hot zone temperature 1400 C. The starting material was NdF_3 of spectral purity grade. The growth was performed in evacuated and sealed platinum ampoule. Temperature gradient inside the heater was 30 K/cm, and the pulling rate was 0.8 mm/hour. As-grown single

crystal samples were of several millimeter size and had several growth facets of rather high optical quality, the latter being varying for different facets. No strange reflections were observed with X-ray. Before measurement, as-grown crystals were polished to produce surfaces with perfect optical quality.

Raman spectra were collected using the polarized radiation of a 488 nm Ar+ laser (Spectra-Physics Stabilite 2017) in the wavenumber region between 10 and 800 cm^{-1}. The spectra were recorded on a Horiba Jobin Yvon T64000 spectrometer. The temperature studies were performed using an ARS CS204–X1.SS closed cycle helium cryostat in the temperature range of 13 – 300K. The accuracy of temperature stabilization during spectra measurement was <0.2 K. The samples for the far IR range was prepared by mixing of melted NdF_3 powder and polyethylene, pellet was made using pellet press. The spectra in the mid-IR range were collected from potassium bromide (KBr) pellet samples, KBr was used instead of polyethylene. The spectra were obtained with Vertex 80V IR spectrometer (Bruker). The temperature studies were performed using an OptistatTM AC-V cryostat in the temperature range of 10 – 286.

Results and discussion

Mechanical representation of the $P–3c1$ trigonal phase at Brillouin zone centre of NdF_3 crystal is:

$\Gamma_{Mech} = 5A_{1g}+5A_{1u}+7A_{2g}+7A_{2u}+12E_u+12E_g$, acoustic and optic modes: $\Gamma_{acoustic} = A_{2u} + E_u$, $\Gamma_{optic} = 5A_{1g}+5A_{1u}+7A_{2g} +6A_{2u}+11E_u+12E_g$, Infrared and Raman active modes $\Gamma_{Raman} = 5A_{1g}+12E_g$, $\Gamma_{Infrared} = 6A_{2u}+11E_u$.

The Raman spectra and mid-infrared spectra of the NdF_3 crystal recorded at ambient condition are shown in Fig. 2 and the frequencies observed are listed in Table 1.

To calculate the NdF_3 vibrational spectrum we used simulation package LADY [11]. Complete spectra of the NdF_3 crystal obtained within the framework of simplified version of the Born-Karman model [12].

Within this model, only the pair-wise interactions and bond-stretching force constants $A = \frac{\partial^2 E}{\partial R^2}$ (E – energy, R – bond length) are considered. Simplified version of the Born-Karman model implies that A depends on R and the $A(R)$ dependencies are the same for all atom pairs:

$$A = \lambda \exp(-r_{ij}/\rho),$$

where r_{ij} is the interatomic distance, and λ and ρ are the parameters characterizing selected pair interaction. To find the parameters of the model the special optimization program was written and tested for several compounds [13-15]. The crystal lattice stability conditions were taken into account. The parameters obtained for NdF_3 crystal are shown in Table 2.

Temperature transformation of Raman spectra is shown in Fig. 3. Crystal cooling leads to reduction of line widths, and to the appearance of the line about 45 cm^{-1}. According to the NdF_3 lattice dynamics calculations three *Eg* mode should appear in the region below 100 cm^{-1}. Two of them are can be clearly seen in Fig. 3 at 36 and 75 cm^{-1} at room temperature. Third line should exits near 50 cm^{-1}. Thus, it can be assumed that the appearing of the line near 50 cm^{-1} can be connected with it intensity increasing. No any significant changes in Raman spectra devoted to the structural phase transitions are observed. The IR spectra of the NdF_3 compound at different temperatures are shown in Fig. 4. It can be seen that, down to 10K, the infrared spectra do not exhibit noticeable changes that could be attributed to structural phase transitions too. Thus, it can be argued that the crystal structure is stable from 300 to 10K.

Conclusion

As a result of these investigations, we can conclude that NdF_3 crystal do not undergo the structural phase transitions in the temperature range 300–10K. No any significant changes in vibrational spectra devoted to the structural phase transitions are observed. The number of active spectral lines is an agreement with the selection rules and the lattice dynamics calculation.

Acknowledgements

This study was partially supported by the Ministry of Education and Science of the Russian Federation and the “Krasnoyarsky regional fund of scientific support and scientific-technical activity”.

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Fig. 1: Structure of NdF_3 crystal: a) projection on the ab plane, b) perspective view

Fig. 2: The Raman spectra and mid-infrared spectra of the NdF_3 crystal

Fig. 3: Temperature transformation of Raman spectra of the NdF_3 crystal

Fig. 4. IR spectra of the NdF_3 crystal at different temperatures

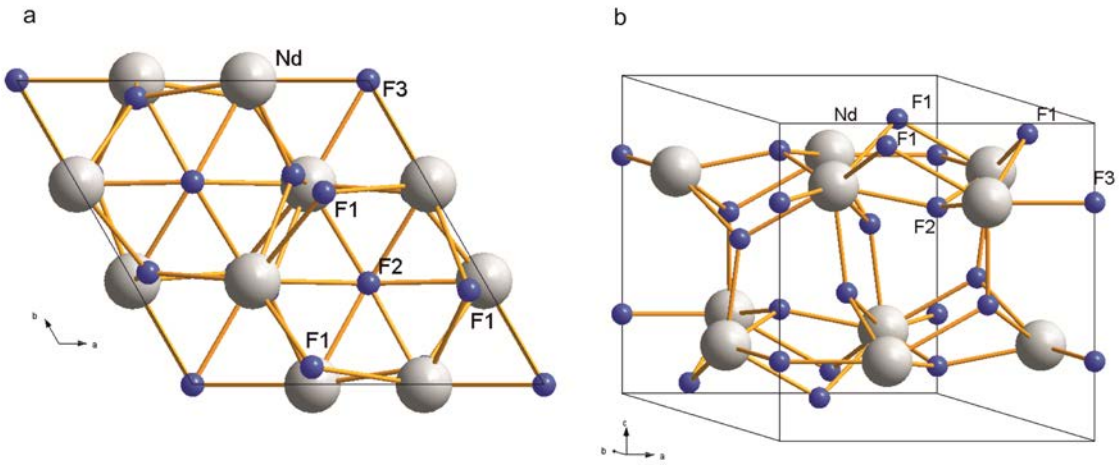

Fig.1.

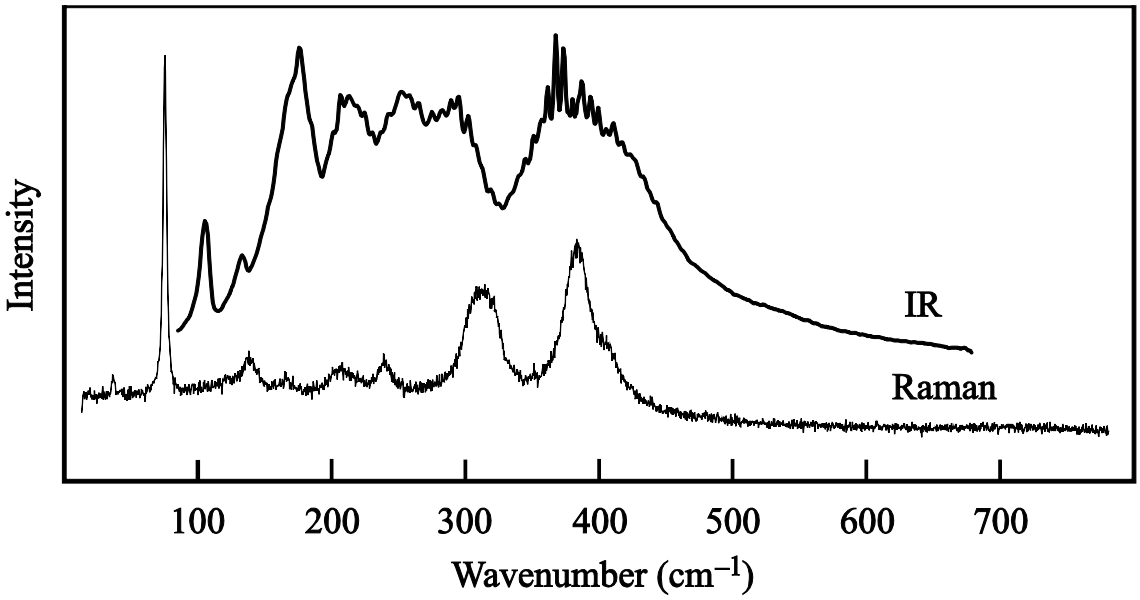
Intensity
IR
Raman
100
200
300
400
500
600
700
Wavenumber (cm−1)

Fig.2.

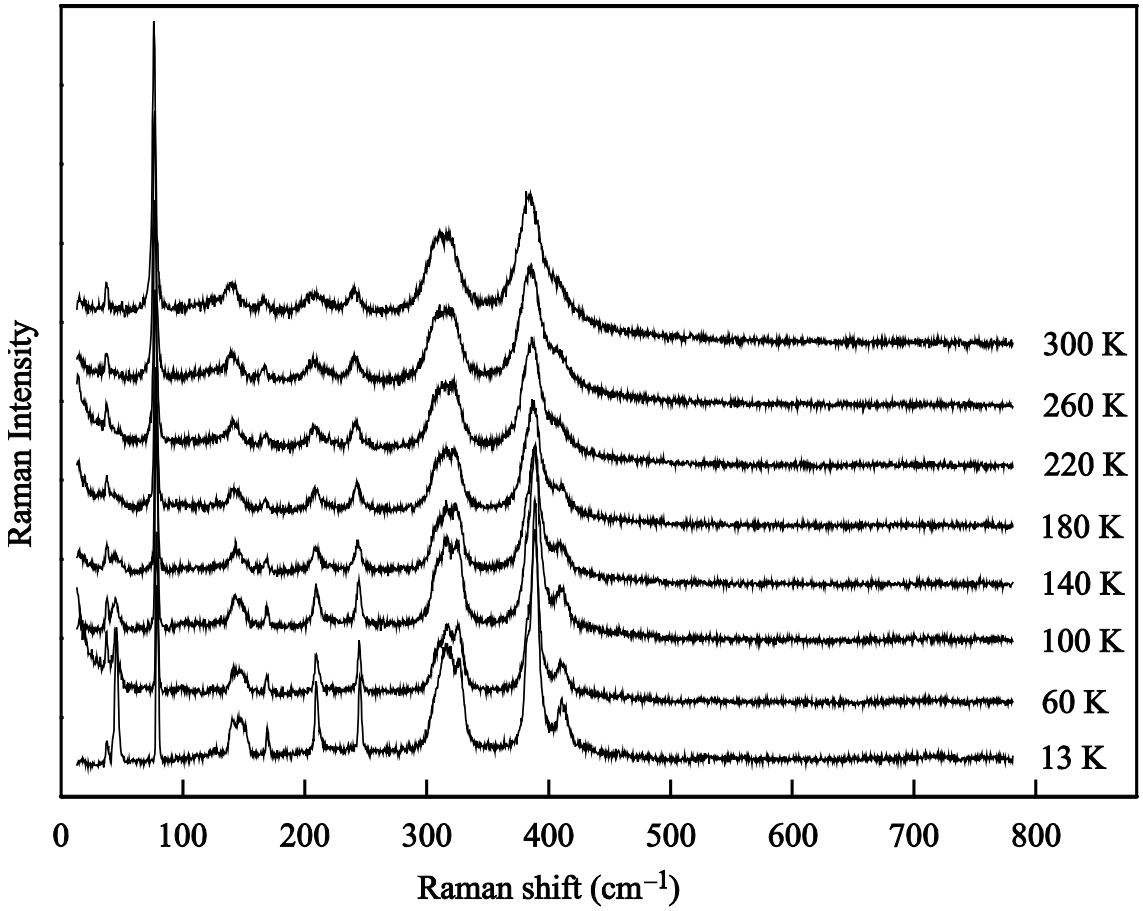
Raman Intensity
300 K
260 K
220 K
180 K
140 K
100 K
60 K
13 K
0
100
200
300
400
500
600
700
800
Raman shift (cm−1)

Fig. 3.

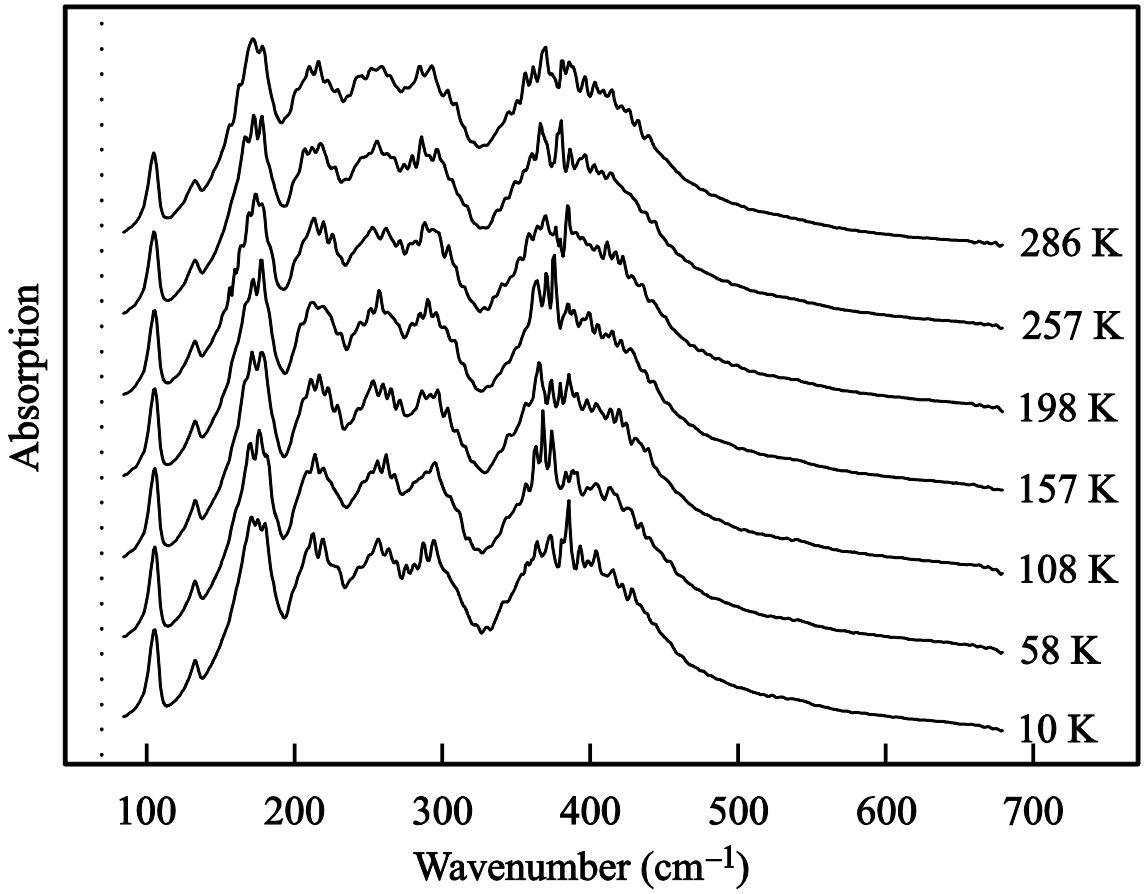
Absorption
286 K
257 K
198 K
157 K
108 K
58 K
10 K
100
200
300
400
500
600
700
Wavenumber (cm−1)

Fig. 4.

Table 1: Experimental and calculated Raman and Infrared frequencies, and band assignments for NdF_3 crystal.

Table 2. Parameters of the interatomic interaction potential.

Symm. Type	Raman exp 13K (cm^{-1})	Raman exp 300K (cm^{-1})	Raman calc. 300K (cm^{-1})	Symm. type	IR exp 300K (cm^{-1})	IR Calc 300K (cm^{-1})
E_g	37	36	36	A_{2u}		38
E_g	45		53	E_u	105	41
E_g	78	75	81	E_u	132	58
A_{1g}	123	120	84	A_{2u}		75
A_{1g}	140	138	129	A_{2u}	163	116
E_g	146		141	E_u	176	121
E_g	151		164	A_{2u}	212	137
A_{1g}	169	165	176	E_u		140
E_g	209	207	181	E_u	253	165
E_g	219		199	E_u		181
E_g	245	240	248	E_u	294	217
A_{1g}	308	306	295	A_{2u}		238
E_g	316		296	E_u	345	252
E_g	327	319	322	E_u	367	295
E_g	382		372	E_u	397	311
E_g	388	384	398	A_{2u}	432	336
A_{1g}	412	407	401	E_u		381

Table 1.

Interactions	λ, aJ/Å^2	ρ, Å
Nd – F1	544.6	0.340
Nd – F2	321.6	0.286
Nd – F3	400.6	0.363
F1 – F1	345.3	0.379
F1 – F2	242.8	0.330
F1 – F3	196.8	0.323

Table 2.